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D₂ and CD₄ Purity Effects on CD Ablators

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Subject: D₂ and CD₄ purity effects on CD ablaters

Overview.

The question of how the isotopic purity of the feed gases D₂ and CD₄ used to make CD ablaters at GA effects the extinction coefficient in the region of wavenumber 2900 cm⁻¹ ($\lambda = 3.45 \mu\text{m}$) is addressed below. The answer is at best incomplete; this is only an interim evaluation. What is clear is that using ultra-pure D₂ is required to lower the "CH" impurity peak at 2900 cm⁻¹. Perhaps using ultra-pure CD₄ also helps, though the evidence for this is mixed. A closer look at the results raises other questions, however, and these are discussed below. Though solving these questions is unlikely to reduce the extinction coefficient in the region of 2900 cm⁻¹ below about 10 cm⁻¹, this work will lead to a better understanding of the deposition of CH/CD GDP, and that is certainly worthwhile.

Experimental Design and Monomer Purity.

In order to focus only on the purity question, depositions were done on salt plates rather than shells. The monomers used and their relative isotopic purity (as per manufacturer) are given in Table 1. In the plots and discussion we will simply refer to isotopic purity as "high" or "low". Table 2 lists in order the experiments run. There are several things to note. First, two samples (a+b) were coated in most cases on sequential days without changes in settings to check reproducibility. The coating thickness was measured on each sample at its center (where the IR beam passes through); the uncertainty in the thickness measurement is at most 0.5 μm . The reason for the large thickness difference in samples 119 is unknown. However all samples were coated for about the same length of time, thus the 35.2 μm value is probably an error. All samples were coated with the same coater, thus variables having to do with different coaters or the relative "dryness" of the coater are removed.

Table 1. Monomers used

species	purity (%D)	
	high	low
D ₂	99.93	99.7
CD ₄	99.97	98.0

Table 2. Experiments

sample number	D ₂	CD ₄ purity	thickness (μm)
030a	low	low	24.1
030b	low	low	24.4
103a	high	high	27.6
103b	high	high	27.1
106a	low	low	27.3
106b	low	low	28.1
110a	high	high	26.1
110b	high	high	27.8
119a	low	high	27.2
119b	low	high	35.2(?)
124a	high	high	25.8
124b	high	high	27.3

Analysis and Discussion.

The collected % transmittance data (% T) was converted to raw absorbance (A) by

$$A = -\ln \left[\frac{\% T}{100} \right]. \quad (1)$$

The baseline was corrected by subtracting the average absorbance between wavenumbers 6000 and 5000 cm^{-1} for each spectrum. In order to take the small variations in thickness into account, the baseline corrected absorbance was divided by the sample thickness in cm. This gives an effective extinction coefficient, ϵ , based on one point and thus assuming that the absorbance at zero thickness is zero. Clearly this method is only a rough approximation, but is adequate for comparisons.

The massaged data is displayed in Figures 1 and 2. There are several key points. First, we can neglect sample 030a; it was inadvertently left in the air for an extended time and clearly has oxidized, the enhanced absorption is due to a broad OH peak. Second, the peak at 3260 cm^{-1} and its shoulder to the right are combination bands of the C-D stretch doublet at 2210 and 2100 cm^{-1} and a sharp C-C vibration at 1055 cm^{-1} . Thus this peak has nothing directly to do with the purity of the feed gases (at least at the levels that we are at) and we see that there is no particular ordering of the samples. However the peak at about 2900 cm^{-1} is due at least in part to C-H vibration. Here (especially clear in the blow up in Figure 2) we see that the low purity gases clearly give a greater absorbance than the high purity gases, indicating an impurity effect. If we assume a "local" baseline of about 15 (the value at 3000 cm^{-1}) then the extinction coefficient reduction of the average of the 3 low purity coatings (not including 030a) to the average of the 6 high purity coatings is about 50%. This is shown in Figure 3.

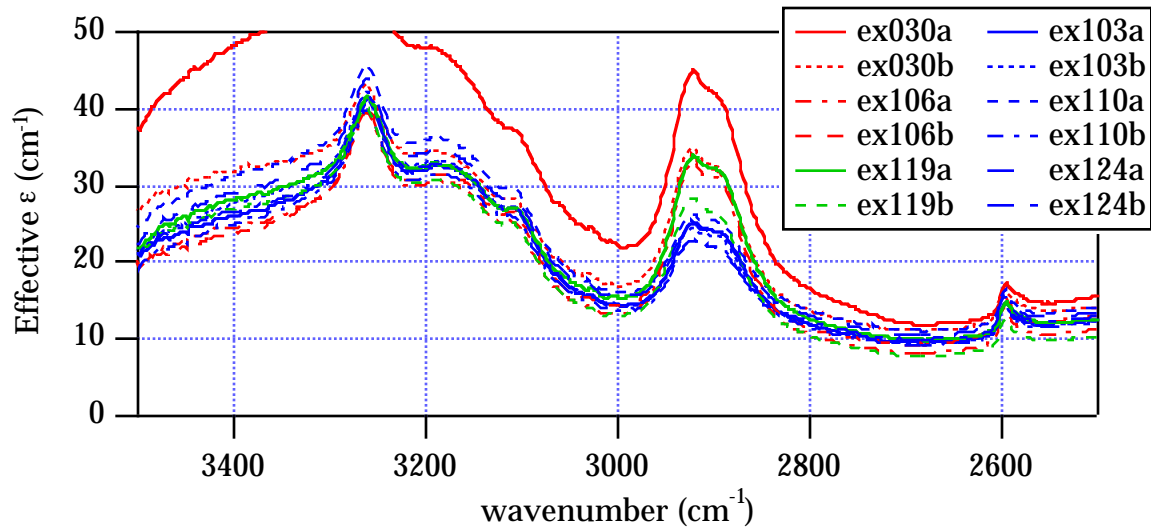


Figure 1. Full set of effective extinction coefficient data between wavenumbers 3500 cm^{-1} and 2500 cm^{-1} (wavelengths 2.86 μm to 4.00 μm)

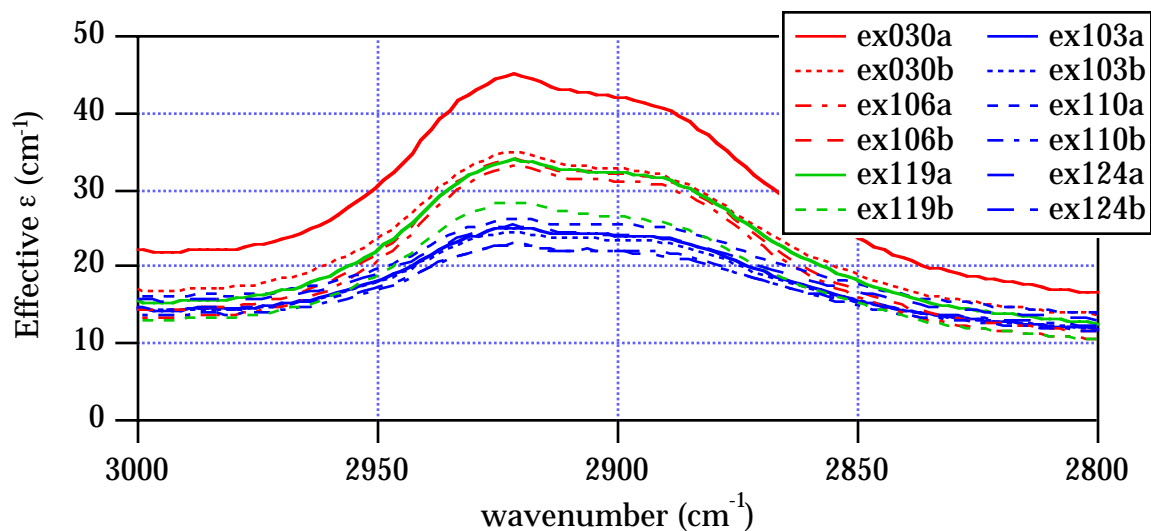


Figure 2. Close-up of the data in figure 1 at the C-H absorption peak at 2900 cm^{-1} . Note that the lower purity gases give consistently higher absorptions.

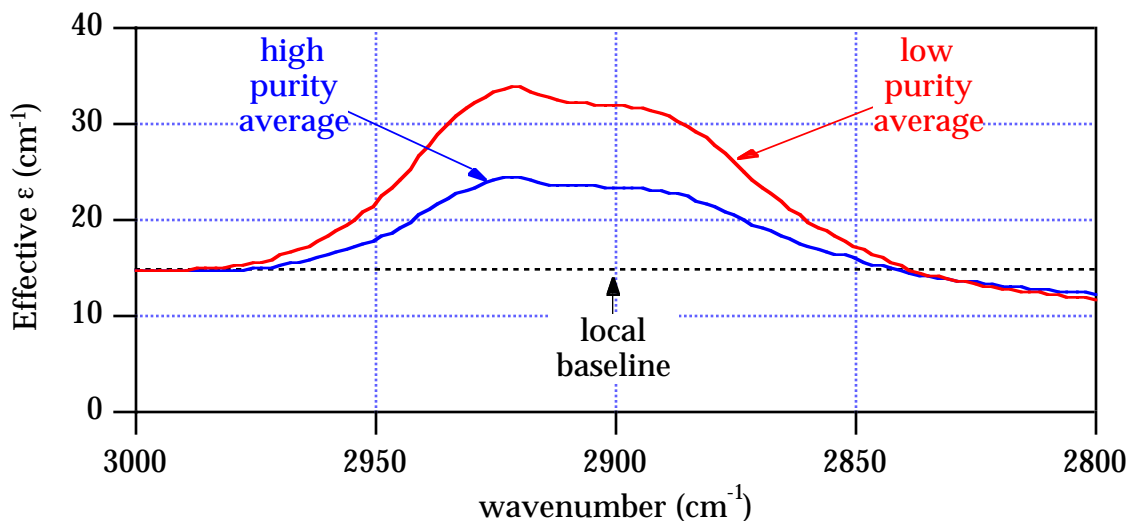


Figure 3. Plot of the average absorption of coatings made from the low purity (not counting 030a) and high purity gases. If one draws a local baseline then the absorption relative to this baseline is reduced by about 50%.

So far so good. But what about the data from runs 119 with low purity D_2 and high purity CD_4 ? If we eliminate the "b" run as being somehow in error, then the results (look only at the solid green data in Figure 2) indicate that the purity of the CD_4 doesn't matter, and that the isotopic purity of the coating is controlled by the D_2 purity. This makes some sense since the D_2 flow dwarfs the CD_4 flow, and if some sort of equilibrium takes place in the plasma before deposition then the D_2 would dominate. Unfortunately in addition to the ambiguity of the "b" run, we didn't do a high purity D_2 with low purity CD_4 run to check this conclusion.

Lastly we need to compare this data with what was previously reported for shells. This is done in Figure 4. There are several observations that can be made (and very few conclusions). First it appears that the new data (red and blue) has a significant high frequency component above 3000 cm^{-1} that was not present in the shell data. This is not a routine baseline correction problem, since the three curves overlay above 4800 cm^{-1} . It looks as if the new data is perhaps contaminated with water. Second, the shell curve in the 3000 to 2800 cm^{-1} region would overlay the red low purity average curve if moved up by 5-6 cm^{-1} . Since the D_2 used in the shell experiments was from a "low" purity batch (though not the same as the D_2 used in these experiments) this is consistent.

So what have we learned? First, it appears that using high purity D_2 cuts the absorbance *due to impurities in the flow gases* by about 50%. However since the improvement in the purity was probably more than 50%[†] there may be some other

[†] In both cases the values listed in Table 1 are minimum purity values, the actual purity was probably high in both cases.

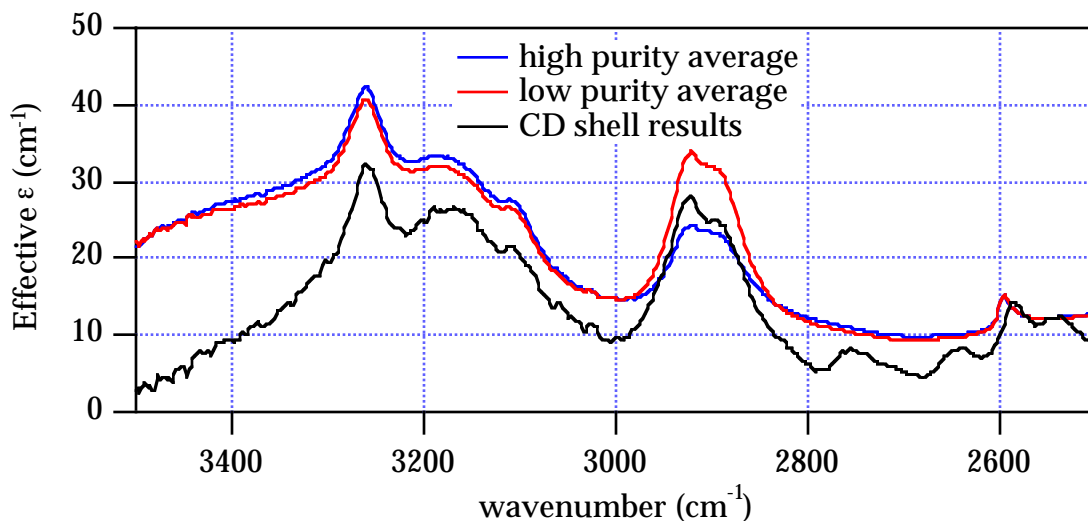


Figure 4. Comparison with previous results from CD shells. There seems to be a water contamination in the new samples, perhaps coming from the salt plates used. However the net amplitude of the peak at 2900 cm^{-1} in shells is similar to that seen for low purity gases.

cause for the peak at 2900 cm^{-1} . Second, the current data may have a constant contamination of water, perhaps on the salt plates themselves. Third, probably the best we can hope for is that the relative peak at 2900 cm^{-1} be completely eliminated. If this were the case there would still be an extinction coefficient of about 8-10 cm^{-1} , presumably due to overtone and combination bands that have nothing to do with isotopic impurities, and thus cannot be removed.

What needs yet to be done? First we need to resolve the problem with possible water contamination. Second it would be worth running a high purity D_2 with low purity CD_4 experiment. But perhaps the key experiment is to repeat the shell experiment with high purity gases. There is one more piece of data that we are investigating, the *rate* of deposition. We find (in one experiment) that coating faster (higher monomer flows) reduces the impurity peak at 2900 cm^{-1} significantly. At this point we have no good explanation for this piece of data, but it will be investigated along with other factors in the near future.